Intersystem Crossing Processes of Acridine

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The $T_1(\pi, \pi^*) \rightarrow T_3(\pi, \pi^*)$ absorption of acridine has first been observed at about 985 nm in ethanol. Temperature dependences of the fluorescence lifetime and the triplet yield of acridine were investigated in poly(vinyl alcohol) film, and it was found that the intersystem crossing from the first excited singlet state $S_1(\pi, \pi^*)$ to $T_1(\pi, \pi^*)$ occurs through both temperature dependent and independent processes. The activation energy of the temperature dependent process corresponds substantially to the energy difference between $T_3(\pi, \pi^*)$ and $S_1(\pi, \pi^*)$. The intersystem crossing from $S_1(\pi, \pi^*)$ to $T_2(n, \pi^*)$ followed by the internal conversion to $T_1(\pi, \pi^*)$ was assigned to the temperature independent process.

Photoreduction of acridine has been studied in various solvents,[1–5] particularly in alcohols in which acridine is fluorescent,[6] and it was suggested that there are two reactive states in alcohols; the first excited singlet state, S_1, and the second excited triplet state, $T_2(n, \pi^*)$.[7–9] However, it is still uncertain whether the reactive singlet state is of π, π^* character or of n, π^*,[10–12] because the energy levels of the $^1(\pi, \pi^*)$ and $^1(n, \pi^*)$ states are close together.[11–13]

The mechanism of the intersystem crossing of acridine from the first excited singlet state to $T_1(\pi, \pi^*)$ has been unknown because of the uncertainty of the energy levels responsible for the intersystem crossing. Recently, Hirata and Tanaka investigated the rise-up of the transient absorption of acridine in ethanol by a picosecond laser technique, and suggested that the intersystem crossing is essentially $S_1(\pi, \pi^*) \rightarrow T_2(n, \pi^*)$ transition followed by $T_2(n, \pi^*) \rightarrow T_1(\pi, \pi^*)$ transition.[14] It was suggested that all of $T_1(\pi, \pi^*)$ is produced through $T_2(n, \pi^*)$ in alcohols.[15]

The energy level of $T_1(\pi, \pi^*)$ was determined experimentally by Evans as 15840 cm^{-1} [16] and that of $T_2(n, \pi^*)$ was calculated by Goodman and Harrell as 21400 or 23500 cm^{-1},[17] while those of the $^1(\pi, \pi^*)$ and $^1(n, \pi^*)$ states are about 26600 cm^{-1} in hydrocarbon solvent.[17] Since the energy difference between the lowest excited singlet state and $T_1(\pi, \pi^*)$ is considerably large, it seems that the intersystem crossing occurs to $T_2(n, \pi^*)$ more easily than to $T_1(\pi, \pi^*)$, particularly if the S_1 state is of π, π^* character.[18]

Bowen *et al.* found that the fluorescence yield decreases with increasing temperature in the ethanol–water mixture.[6] The triplet yield of 9-methylacridine increases with increasing temperature in ethanol.[11] These earlier observations suggest that acridine is subject to temperature dependent intersystem crossing similar to the 9,10-disubstituted anthracenes.[19–22]

In order to clarify the mechanism of the intersystem crossing of acridine, we have measured the T-T absorption spectrum in the near infrared region and studied the temperature dependences of the fluorescence lifetime and the yield of $T_1(\pi, \pi^*)$ in poly(vinyl alcohol) film (PVA), where the photoreduction is negligible and the S_1 state seems to be a $^1(\pi, \pi^*)$ state.

Experimental

Materials. Acridine (C. P. grade, Tokyo Kasei) was recrystallized from the ethanol–water mixture after pretreatment with activated charcoal in ethanol. Ethanol (G. R. grade, Wako Jun-Yaku) and poly(vinyl alcohol) (the degree of polymerization 1400, Koso Kagaku) were used without further purification.

Apparatus and Procedure. The absorption spectrum was measured with a Hitachi EPS-3T spectrophotometer, and the fluorescence spectrum with a modified Hitachi EPU spectrophotometer. Lifetime measurement was made with a phase-fluorometer modulated at 10.7 MHz. Relative yields of the triplet acridine and the T-T absorption spectra in the visible region were measured with an ordinary flash apparatus. The T-T absorption spectrum in the near infrared region was measured by the use of the combination of a HTV R-406 photomultiplier and an Ushio JC-12-130 L halogen lamp as a monitoring light source. Absolute yield of the triplet acridine was determined by the use of a flash irradiation apparatus as shown in Fig. 1.

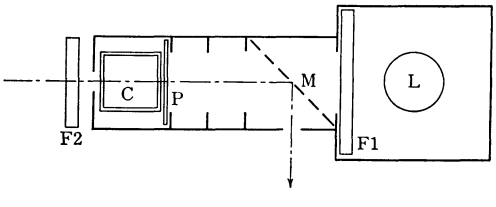

Fig. 1. The flash irradiation apparatus used to determine the intersystem crossing probability of acridine in PVA.
L: Xenon flash lamp, F_1: Hoya U 2 band path filter, M: half mirror, P: PVA film, C: actinometer cell, F_2: Toshiba V-Y 43 cut off filter.

Results and Discussion

The absorption and fluorescence spectra of acridine in PVA are shown in Fig. 2, from which the energy level of $S_1(\pi, \pi^*)$ is estimated to be 25450 cm^{-1} as an average of the absorption maximum in the ^1L_a band at 25900 cm^{-1} and the fluorescence maximum at 25000 cm^{-1}.[23] Figure 3 shows the T-T absorption spectra of acridine in PVA and ethanol. The absorption maxima in the near infrared region lie at 10150, 11500, and 12850 cm^{-1} in ethanol. Since no transient absorption was observed below 9800 cm^{-1}, the absorption at 10150 cm^{-1} was assigned to the 0-0 band of the $T_1(\pi, \pi^*) \rightarrow T_3(\pi, \pi^*)$ transition. Hence the energy level of $T_3(\pi, \pi^*)$ is estimated to be 25990 cm^{-1}.

The fluorescence lifetime in PVA is 8.2_6 ns at 13 °C. Since the rate constant of the fluorescence emission, k_f, is estimated to be 3.6×10^7 s^{-1} from the known values of

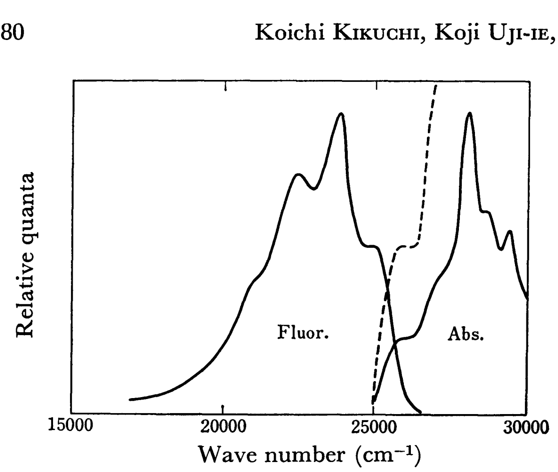

Fig. 2. The absorption and fluorescene spectra of acridine in PVA.

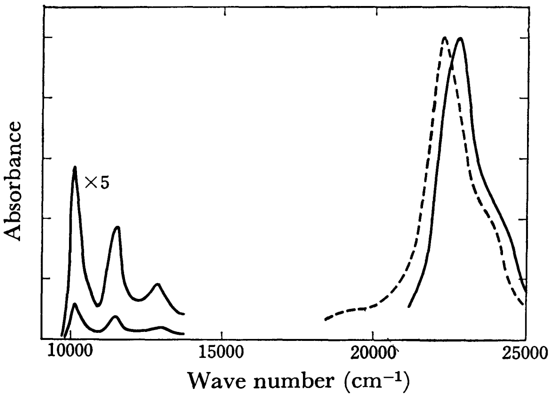

Fig. 3. The T-T absorption spectra of acridine in PVA (-----) and in ethanol (——).

the fluorescence yield ($\phi_f=0.37$)[6] and the lifetime (10.3 ns)[24] in water, the fluorescence yield in PVA is evaluated as 0.30 at 13 °C. The large yield and the long lifetime imply that the S_1 state is a $^1(\pi, \pi^*)$ state in PVA.

According to a method similar to that in a previous paper,[15] the intersystem crossing probability of acridine from $S_1(\pi, \pi^*)$ to $T_1(\pi, \pi^*)$ was determined to be 0.56 in PVA at 23 °C by the use of the molar extinction coefficient of the T-T absorption maximum in ethanol, $\varepsilon_T=18500\ M^{-1}\ cm^{-1}$ at 440 nm.[25]

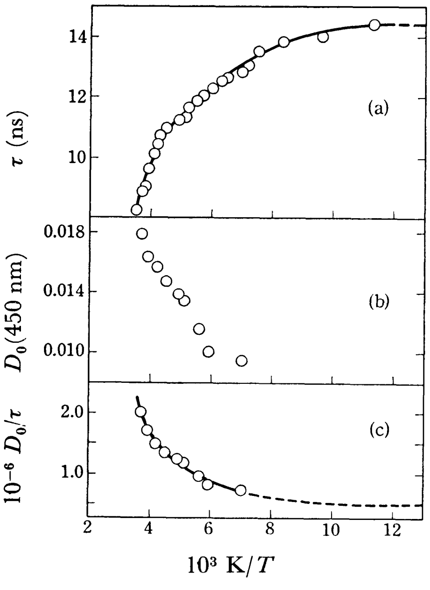

Fig. 4. The temperature dependencies of the fluorescence lifetime (a), the absorbance of the T-T absorption immediately after flashing (b), and their ratio (c).

Figure 4 shows the temperature dependences of the fluorescence lifetime (τ), the absorbance (D_0) of the T-T absorption immediately after flashing, and the ratio (D_0/τ). The lifetime increases with decreasing temperature and approaches to about 14 ns at low temperature. On the other hand, D_0/τ which is associated with the rate of intersystem crossing, decreases with decreasing temperature. It is obvious that both the decay of the singlet excited state and the intersystem crossing occur through temperature dependent and independent processes. When the extrapolated values of $1/\tau$ and D_0/τ at lower temperature are subtracted from their original values, the resulting Arrhenius plots are linear as shown in Fig. 5, and their slopes are nearly the same; the apparent activation energy is estimated to be 420 cm^{-1}. Therefore, we can safely conclude that both the deactivation of $S_1(\pi, \pi^*)$ and the production of $T_1(\pi, \pi^*)$ occur through two kinds of processes; one is temperature dependent and the other is temperature independent.

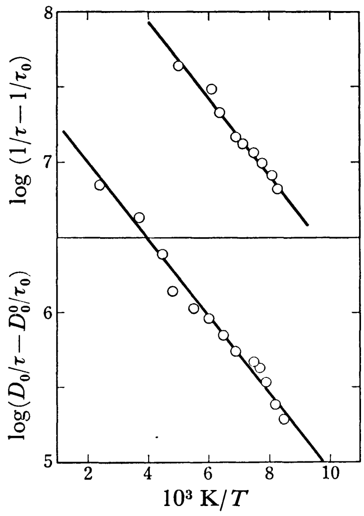

Fig. 5. The Arrhenius plots of $(1/\tau-1/\tau_0)$ and $(D_0/\tau-D_0^0/\tau_0)$ *vs.* temperature.

The energy difference between $S_1(\pi, \pi^*)$ and $T_3(\pi, \pi^*)$ is nearly equal to the activation energy, so that the temperature dependent process seems to be the intersystem crossing from $S_1(\pi,\pi^*)$ to $T_3(\pi,\pi^*)$. In the case of acridine, there are two low-lying triplet states, $T_1(\pi,\pi^*)$ and $T_2(n,\pi^*)$. According to the spin-orbit coupling selection rule of El-Sayed[18] and the energy gap law,[26] the $S_1(\pi,\pi^*)\rightarrow T_2(n,\pi^*)$ transition would be much easier than the $S_1(\pi, \pi^*)\rightarrow T_1(\pi, \pi^*)$ transition. This view coincides with the suggestions that $T_1(\pi, \pi^*)$ is mainly produced through $T_2(n,\pi^*)$ in alcohols,[15] and that the first step of the intersystem crossing is $S_1(\pi,\pi^*)\rightarrow T_2(n,\pi^*)$ transition in ethanol.[14]

On the basis of the above informations, we propose a Jablonski diagram as shown in Fig. 6, where k_d is the rate constant of non-radiative transitions other than intersystem crossing. According to the diagram, the

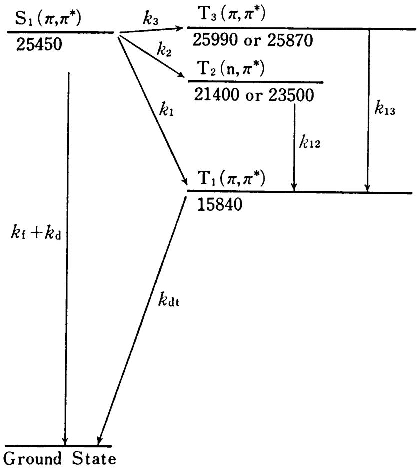

Fig. 6. The Jablonski diagram of acridine in PVA.

fluorescence lifetime and the yield of $T_1(\pi, \pi^*)$ are expressed as follows;

$$\tau = 1/(k_f+k_d+k_1+k_2+k_3), \tag{1}$$

$$\phi_{ST} = (k_1+k_2+k_3)\tau. \tag{2}$$

D_0 is related to the light absorbed during flashing, I_{ab}, as follows;

$$D_0 = \varepsilon_T[T]_0 d = \varepsilon_T d\cdot\phi_{ST} I_{ab}, \tag{3}$$

where $[T]_0$ is the triplet concentration immediately after flashing and d is the thickness of PVA. At sufficiently low temperature, following relations hold;

$$\tau_0 = 1/(k_f+k_d+k_1+k_2), \tag{4}$$

$$\phi_{ST}^0 = (k_1+k_2)\tau_0, \tag{5}$$

$$D_0^0 = \varepsilon_T d\cdot\phi_{ST}^0 I_{ab}. \tag{6}$$

Putting $k_3 = k\exp(-\Delta E/RT)$, we obtain the following equations from Eqs. 1—6;

$$\frac{D_0}{\tau} - \frac{D_0^0}{\tau_0} = \varepsilon_T d I_{ab} k \exp\left(-\frac{\Delta E}{RT}\right), \tag{7}$$

$$\frac{1}{\tau} - \frac{1}{\tau_0} = k\exp\left(-\frac{\Delta E}{RT}\right). \tag{8}$$

These equations can analyze the results shown in Fig. 5, and the following values are obtained;

$$\frac{1}{\tau_0} = 7\times 10^7\,\text{s}^{-1},$$

$$k = 3.7\times 10^8\,\text{s}^{-1},$$

$$\Delta E = 420\,\text{cm}^{-1},$$

$$\varepsilon_T(450) d I_{ab} k = 1.3\times 10^7\,\text{s}^{-1},$$

$$\frac{D_0^0}{\tau_0} = \varepsilon_T(450) d I_{ab}\cdot(k_1+k_2) = 5\times 10^5\,\text{s}^{-1}.$$

From the last two relations, the rate constant of the intersystem crossing to the two lower triplet states, k_1+k_2, was calculated to be $1.4\times 10^7\,\text{s}^{-1}$.

All of the rate constants involved in the Jablonski diagram were summarized in Table 1. The yield of $T_1(\pi, \pi^*)$ in PVA at any temperature can be calculated by the following relation derived from the above results;

$$\phi_{ST} = (k_1+k_2+k_3)\tau = \frac{0.20+5.3\times\exp(-604/T)}{1.0+5.3\times\exp(-604/T)}. \tag{9}$$

Table 1. Rate constants of the deactivation of excited acridine

$k_f = 3.6\times 10^7\,\text{s}^{-1}$	
$k_d = 2.0\times 10^7\,\text{s}^{-1}$	
$k_3 = 3.7\times 10^8 \times \exp\left(-\frac{\Delta E}{RT}\right)$	$\Delta E = 420\,\text{cm}^{-1}$
$k_1+k_2 = 1.4\times 10^7\,\text{s}^{-1}$	$k_1 \ll k_2$
$k_{dt} = 4.2\times 10\,\text{s}^{-1}$	

From Eq. 9, we get $\phi_{ST}=0.53$ at 23 °C, which agrees satisfactorily with the experimental value 0.56. Such agreement between the calculated and observed values supports strongly the validity of both the deactivation pathways shown in Fig. 6 and their rate constants cited in Table 1. The fluorescence and intersystem crossing yields at sufficiently low temperature are calculated to be 0.51 and 0.20, respectively.

In the above discussion, the contribution of the $^1(n, \pi^*)$ state to the deactivation of $S_1(\pi, \pi^*)$ has been ignored. The value of k obtained is the same order of magnitude for the frequency factor of a intersystem crossing process in aromatic hydrocarbons;[27] there seems to be no enhancement of the intersystem crossing due to the spin-orbit coupling between the $^1(n, \pi^*)$ state and $T_3(\pi, \pi^*)$. Therefore, it is probable that the energy level of the $^1(n, \pi^*)$ state is too high to play an important role in the intersystem crossing.

In this study, it has first been confirmed that there are two kinds of processes in the intersystem crossing of acridine from $S_1(\pi,\pi^*)$ to $T_1(\pi,\pi^*)$ in PVA; the temperature dependent process through $T_3(\pi,\pi^*)$ whose energy level is about 420 cm^{-1} higher than that of $S_1(\pi, \pi^*)$ and the temperature independent processes in which the path through $T_2(n, \pi^*)$ seems to be most important.

As regards k_d, the internal conversion is unreasonable because of the large energy gap between $S_1(\pi, \pi^*)$ and the ground state. Although the quantum yield of photoreduction of acridine by steady light illumination is very small in PVA, the weak transient absorption other than the T-T absorption was observed at about 560 nm where acridine radicals have the absorption.[28] Therefore, the non-radiative process may be due to the transient reaction in $S_1(\pi, \pi^*)$.

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